

PATENT SPECIFICATION

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(54) MICROWAVE DRYING PROCESS FOR SYNTHETIC POLYMERS

(71) We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organized and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to improved polymer processes. More specifically, it relates to improved devolatilizing and drying techniques utilizing microwave heating.

In conventional processes for making polymers, it is necessary to remove solvents and/or water from the polymer. For example, in the preparation of butyl rubber, the product is recovered as a slurry of butyl rubber, generally in the form of crumbs, in the water. The rubber crumb is then removed from the slurry and dewatered on a vibrating screen or Oliver type rotary filter to about 30 to about 60% water by weight. It is further mechanically dewatered, e.g. using an Anderson Expeller or dewatering extruder, to a water content of about 6 to about 20 wt %.

An Anderson Expeller is a continuous mechanical screw press employing discontinuous worms on a shaft separated at intervals by collars and breaker lugs and operating within and through a barrel made up of bars separated by thin spaces. The shaft moves the material from the hopper, through the drainage barrel. As the solids move through the barrel under pressure, the liquid is pressed from the solids and permitted to escape through spaces between the bars that make up the barrel.

Thereafter, the remaining water is removed by heating. For example, the crumb is fed into a heated devolatilizing extruder equipped with a die face pelletizer. The pellets so formed are substantially free, i.e. 0.1 to 0.5

wt. %, of water. They are then dropped into the water to cool to prevent agglomeration of the pellets. The surface water is removed by heating in a drying tunnel. The pellets are then cooled and baled, under pressure, in known manner.

The baling process is generally performed at a temperature of about 140°F. to about 250°F. and a pressure of about 800 to about 3500 psig; the heat and pressure being maintained for about 5 to about 60 seconds. The resulting compacted mass has a density of about 40 to about 54 pounds per cubic foot.

Similar processes incorporating water separation and drying steps are inherent in other polymer processes. For example, styrene butadiene (GR-S) rubber is prepared as a rubber latex which is coagulated by the addition of acid or salts. The coagulated product is washed, filtered on an Oliver rotary vacuum drum filter, from which it is removed, having a water content of about 30 wt. % and dried for about two hours at a maximum of 82°C. to reduce the volatile matter content (i.e. water) to about 0.5 wt. %.

It is readily evident that large space requirements and equipment costs are needed in these conventional drying operations. Additionally, in certain processes, the heating steps are either inadequate or detrimental.

For example, the shearing action and high temperature in the devolatilizing extruder, i.e. 375—500°F., results in polymers (e.g. PVC, butyl rubber) having molecular weight distributions skewed toward the low end. Consequently, it is only with great difficulty that, in preparing butyl rubber, can a polymer be prepared which has a ratio of number average molecular weight (M_n) to weight average molecular weight (M_w) greater than 4.0.

The halogenated butyl rubbers, especially brominated butyl rubber, for example, decompose at the drying temperatures used in the devolatilizer extruder. The result is the

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release of lacrimatory gases, e.g. HBr, and severe corrosion of equipment.

When polyisobutylene has been prepared and dried in a conventional manner, baled in the manner described in U.S. Patent 3,264,387 and stored for several weeks, the bales become relatively transparent. Occluded moisture becomes visible as a large white "baseball" in the center of the bale.

Though the polymer water content is only about 0.1 to about 0.8 wt. %, and does not affect product quality, the appearance of the bale affects customer acceptance. It is desirable therefore to remove this remaining water to give a moisture-free product. Conventional drying techniques are inadequate to further reduce the water content of the polymer.

Various polymer processing techniques have been developed utilizing electronic heating. For example, metal particles have been dispersed in a vulcanizable rubber and the mix cured by induction heating at a frequency of about 1 MHZ (megahertz) e.g. see U.S. 3,249,658. As the name implies, induction heating operates by inducing a current in a conductor, i.e. metal filings; the heat effect depends on the eddy currents induced in the material and the heating of the rubber is by conduction from the metal filings.

Dielectric heating has been used to heat non-conductors having polar molecules. For example, polyvinyl chloride may be pressed into molding "pre-forms" and heated by dielectric heating prior to introduction into a compression mold. This heating technique relies on the polarity of the molecule to induce a heating effect. The material to be heated is placed between two plates which form a capacitance in an electronic circuit. The polarity of the plates is rapidly reversed at a frequency in the range of about 1 to about 150 MHZ. Heating is caused by the rapid vibration of the polar molecules attempting to align themselves with the constantly changing field.

More recently the partial curing of natural rubber or synthetic elastomers has been accomplished by passing the material through the center of a tubular wave guide which is connected to a microwave generator running at 300 to 30,000 MHZ, e.g. British Patent 1,065,971. Curing is completed by passing the material through a conventional heater.

Microwave heating, like conventional dielectric heating, is based on the principle that electromagnetic waves interact with a dielectric material, some of the energy associated with these waves being stored and some being dissipated. The heating effect is a function of the dissipated energy (dielectric loss). The dielectric loss is caused by the frictional drag associated with permanent or induced dipole orientation in the alternating electric field. Generally, polymers show an

increase in dielectric loss with an increase in frequency of the radiation. Some polymers, however, e.g. PVC, actually show a decrease in dielectric loss at the higher frequencies.

Though all polymer molecules exhibit some polarity, with few exceptions, the synthetic elastomers are essentially nonpolar and hence, have a low dielectric loss. Heating of these materials is usually accomplished by the inclusion of polar materials such as fillers, i.e. carbon black.

In accordance with the present invention there is provided a process for removing a polar vehicle (as defined) from an essentially non-polar synthetic polymer containing the polar vehicle which comprises:

a) transferring the synthetic polymer containing the polar vehicle to a conveying means; and

b) passing said polymer by means of said conveying means through at least one microwave resonating cavity operating at a microwave frequency of 900 to 30,000 MHZ for a period of time sufficient to reduce the polar vehicle content of said polymer to less than 5,000 ppm.

Preferably, the polymer is passed through two microwave resonating cavities, the first operating at a microwave frequency of 915 MHZ and the second operating at microwave frequency of 2450 MHZ, the period of time in the first cavity being sufficient to reduce the vehicle content of the polymer to less than 5 wt. % and the period of time in the second cavity sufficient to reduce the vehicle content of the polymer to less than 5,000 ppm.

Desirably, the polymer is passed through the cavity or cavities for a time sufficient to reduce the polar vehicle content of the polymer to less than 10 ppm.

Suitably, the synthetic polymer when transferred to the conveying means has a polar vehicle content of 6-30 wt. %. The polymer may be a slurry in the polar vehicle. Normally, when the synthetic polymer is polyisobutylene it is preferred that it is in particulate form and has a moisture content, when transferred to the conveying means, of less than 5 wt. % (desirably 0.1 to 0.8 wt. %); and the time in resonating cavity is sufficient to reduce the moisture content to less than 1 ppm. The thus dried polyisobutylene can thereafter be baled by compressing the polymer at a temperature of 140-250°F and a pressure of 800-3500 psig for 5-16 seconds.

It is to be understood that, unless otherwise stated, in this specification and claims all parts are parts by weight.

During a preferred drying process, the wet polymer is carried through a resonating cavity on a conveyor belt, the polymer forming a bed on said belt of three to seven inches in depth. It is also preferred in processes according to

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the invention that the polymer is in particulate form.

Surprising added advantages of this drying technique are that the polymers dried by the process of this invention have improved appearance, a broader molecular weight distribution (i.e. higher M_n), and a higher modulus of elasticity. Further, though the polymer is thoroughly dry, it leaves the second resonating cavity only warm to the touch and requires no further cooling before balancing.

The present invention will be further illustrated by reference to the drawings in which:

Fig. 1 is a flow diagram of a preferred method for carrying out the process of this invention; and

Fig. 2 is a schematic isometric detail of a resonating cavity (microwave oven).

The expression "butyl rubber" as used herein is well known in the art. See for example, Industrial Engineering and Chemistry, Vol. 32, pp. 1283 et seq.

The butyl rubber generally has a Staudinger molecular weight of approximately 20,000 to 500,000; preferably 25,000 to about 200,000; especially 45,000 to 60,000; and a Wij's iodine number (A.S.T.M.D.-460) of 0.5 to 50; preferably 1 to 15. The preparation of butyl rubber is described in U.S. Patent 2,356,128.

Halogenated rubbery isoolefin-multiolefin-containing copolymers, particularly brominated butyl rubber, which are advantageously devolatilized and dried in accordance with the present invention, are preferably produced by halogenation of the rubbery isoolefin-multiolefin copolymers in a manner which does not degrade the molecular weight thereof by techniques well known in the art, such as the method of U.S. Patent No. 2,944,578.

The resulting halogenated butyl rubber may be recovered by precipitation with oxygenated hydrocarbons, particularly alcohols or ketones such as acetone or any other known non-solvent for the halogenated butyl rubber and dried at 1 to 760 millimeters or higher of mercury pressure absolute, at 0° to 180°C., preferably at about 50° to 150°C., e.g. 70°C. Other methods of recovering the chlorinated polymer are by conventional spray or drum drying techniques.

Alternately, the solution of the halogenated rubber may be injected into a vessel containing steam and/or agitated water heated to a temperature sufficient to volatilize the solvent and form an aqueous slurry of the rubber. This halogenated rubber may be separated from the slurry by filtration and recovered as a crumb. As so produced, the halogenated rubbery polymer has a Staudinger molecular weight within the range of approxi-

mately 20,000 to 500,000, preferably 25,000 to 200,000.

The term "polyisobutylene" as used in this specification is intended to mean homopolymers of isobutylene having a Staudinger molecular weight of approximately 60,000 to about 140,000. The particular polymerization techniques by which the polymer is made does not form an essential part of this invention.

Though GR-S type (styrene butadiene) latex is referred to in particular, it is obvious the drying technique of this invention is applicable to any latex polymerization process. The term "latex polymerization" as used in this specification includes any process in which monomers are emulsified into or suspended in a water medium during the polymerization process. The term "latex" as used in this specification includes all polymers formed by latex polymerization techniques.

The term "microwave heating" as used throughout this specification means heating with electromagnetic radiation at 900 to 30,000 MHZ. Preferably, the microwave heating frequency is 900 to 8600 MHZ, more preferably 915 to 2450 MHZ.

Though application of this invention is directed primarily toward particular synthetic elastomers, it is evident that the invention disclosed herein is suitable for use in any process for making of essentially non-polar polymer which requires a drying step to remove volatile polar solvents or water. The term "polymer" includes elastomers, plastimers, and thermoplastics. The term "essentially non-polar" includes those materials having a dielectric loss factor of 0.0001 to about 0.1, e.g. butyl rubber, halogenated butyl rubber, GR-S polymers and polyvinyl chloride.

In operating the process of the invention, for example in the drying of butyl rubber, the depth of the rubber on the conveyor belt can be about five to about ten inches, preferably six to eight inches, e.g. seven inches, at 915 MHZ; and about one to three inches, preferably 1½ to 2½ inches, e.g. two inches, at 2450 MHZ.

Referring now to the drawing and particularly to Fig. 1, a numeral 11 designates a discharge line from the slurry tanks of a butyl rubber operation by means of which the aqueous slurry is transferred to a vibrating screen 12. The bulk of the water is separated from the butyl rubber crumb, the water being discharged by water discharge line 13 and the crumb containing about 60% water is transferred by means of a screw conveyor 14 to an Anderson Expeller, 15, which reduces the water content to 6 to 30 wt %, usually 10 to 20 wt %, the water being discharged through water discharge line, 13'. The crumb, reduced in water content, is discharged onto a conveyor belt 16 and carried into the first resonating cavity 17 which has introduced into it, by means of a wave guide

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Latex

18, electromagnetic radiation at 915 MHZ. The water content is reduced to about 5 wt. %. Thereafter, the material passes into the second resonating cavity 19 which has introduced into it, by means of a wave guide 20, electromagnetic radiation at 2450 MHZ. The butyl rubber crumb is discharged from the second resonating cavity 19 with a water content less than ten parts per million (ppm), e.g. less than one ppm.

The resonating cavities, 17 and 19, may be two separate microwave ovens each equipped with inlet and outlet absorption barriers or it may be a single unit with the two cavities separated by a metal barrier wall and appropriate microwave isolators 27 (e.g. 5-25 inch water filled space).

The structure of the resonating cavity may be more clearly understood by referring to the drawing, in particular Fig. 2, wherein numeral 21 designates an enclosure (the resonating cavity) constructed of electrically conductive material (e.g. metal). The enclosure is five to ten feet long, one to four feet high and about two to four and one-half feet wide; the dimensions are dependent on the amount of material to be treated, the contemplated power input and the desired residence time. The inlets for the microwave radiation, 22, 23 and 24, are preferably located in the corners of one end of the enclosure, 21, and directed at right angles to one another. At least one of the inlets, 22, is directed countercurrent to the flow of material in the cavity.

At each end of the enclosure is an opening; an outlet 25 and an inlet 26. Radiation of microwave out of these openings is suppressed by means of filters consisting of reactants, the design of which is well known to the art or by an absorbing barrier, 27, such as water or ethylene glycol. The absorption medium is cooled by circulation through an external heat exchanger, 28.

The conveyor belt, 29, is supported within the enclosure, 21, by equally spaced rollers, 30, made of non-conducting material such as "Teflon" (TEFLON is a registered Trade Mark) or ceramics.

To prevent condensation within the enclosure, warm air is blown across the material to be dried. The air inlets, 31, and outlets, 32, being so located as to best utilize the air flow. For example, in the drying of butyl rubber the conveyor belt, 29, is a screen. The air inlets, 31, are located below the screen and the outlets, 32, in the side of the enclosure, necessary baffles being provided to prevent short cutting of the flow. The air flow is up through the bed of butyl rubber and out through the outlets. For powdery material such as latices, the flow is across the surface from one side of the belt to the other.

The microwave radiation inlets are coupled to a microwave generator in the conventional

manner through wave guides. In order to insure uniform distribution of radiation throughout the cavity, mode stirrers, 33, are located at the end of the enclosure opposite the radiation inlets. The stirrers generally consist of a rotatably mounted bar, 34, and two diametrically opposed paddles, 35, extending the length of the bar. In operation, the adjacent stirrers are 90° out of phase with one another (i.e. in their rest position the blades of adjacent stirrers are at right angles to one another). One to ten such stirrers are used; preferably three to five stirrers.

The following examples serve to illustrate the manner in which the process of this invention may be carried out as well as the benefits derived therefrom.

EXAMPLE 1

Drying of butyl rubber having an average moisture content of 20 wt. %.

Equipment:

1. A resonating cavity operating at 915 MHZ (L-band)

Cavity dimensions: width—4 ft.; height—3 ft.; length—30 ft.

Conveyor belt width: 3 ft.

Power (microwave): 450 KW

Air flow rate: 1500 CFM at 170°F.

2. Two resonating cavities each operating at 2450 MHZ (S-band)

Cavity dimension: width—4 ft.; height—3 ft.; length—15 ft.

Conveyor belt width: 3 ft.

Power (microwave): 90 KW per cavity

Air flow rate: 1300 CFM at 150°F.

Butyl rubber crumb leaving the Anderson Expeller of a butyl rubber plant, having a water content of about 20 wt. %, was fed on to the conveyor belt of the L-band cavity at a rate of about 6350 pounds per hour (wet). The crumb bed height was about six inches. After a residence time of about 90 seconds (controlled by belt speed), the crumb exited from the L-band cavity with a water content of 5 to 7 wt. %.

This partially dried product was split into 2 streams and fed into the S-band cavities. The depth of the bed in these units was about 1½ inches. After about a 12½ second residence time within the cavity, the rubber emerged with a water content of less than ten ppm and a snow white appearance. Production rate was about 5000 pounds per hour of dry polymer.

EXAMPLE 2

One of the S-band cavities of Example 1 was operated at 120 KW microwave power and used to dry about 4000 pounds per hour of wet polyisobutylene.

A. Polyisobutylene having a water content

of about 5 wt. % was dried to a water content of less than one ppm after a residence time in the cavity of about 25 seconds.

B. Polyisobutylene having a water content of about 2 wt. % was dried to a water content of less than one ppm after a residence time in the cavity of about ten seconds.

When the polyisobutylene of this example is baled, the bale remains clear and there is no observable indication of occluded water, i.e. white "baseballs."

EXAMPLE 3

In a laboratory-scale test, polyvinyl chloride containing about 18 wt. % water was dried in an S-band (2450 MHZ) cavity utilizing 60 KW microwave power. The conveyor belt width was twelve inches, the air inlet temperature was 145°F. and the air flow rate was about 1300 CFM. The product bed height on the conveyor was about 2 inches while the residence time was about 25 seconds.

The product produced at 50 pounds per hour had a final water content of less than one ppm. Its appearance was snow white in color and hence, would produce a film of greater clarity than the usual off-white product.

A determination of the molecular weight (vapor phase osmometry) was made and found to be 10,000 as compared to 8,000 for the conventionally dried powder.

Though in actual practice such large quantities of water (i.e. >5 wt. %) would be removed using both an L-band and S-band cavity in series, this laboratory experiment serves to demonstrate that, surprisingly, drying by microwave heating results in a product having improved appearance and higher molecular weight.

EXAMPLE 4

In a polypropylene process the polymer, containing about 25 wt. % atactic polypropylene and about 13 wt. % water, was dried in the laboratory unit of Example 3. After a residence time of about sixteen seconds, the product (50 pounds per hour) had a snow white appearance and a water content of less than one ppm.

EXAMPLE 5

Butyl rubber crumb having a water content of about 5% was dried in one of the S-band cavities of Example 1 operating at 90 KW microwave power. The crumb bed height was about 1½ inches while the air flow rate was 1400 CFM at a temperature of about 145°F. A residence time of about 30 seconds reduced the water content to less than one ppm. The product (4000 pounds per hour weight) was snow white in the form of crumbs and when baled was clear rather

than off-white or amber as is the conventionally dried material.

The product had a broader molecular weight distribution (i.e. $\frac{M_w}{M_n} = 6$, vs. 4 for conventionally dried rubber). The broader molecular weight range makes for a more easily processed rubber.

The above example serves to illustrate that the drying of butyl rubber by microwave heating techniques results not only in greatly reduced drying time as anticipated, but, surprisingly, produces a product having improved appearance and broader molecular weight distribution.

Although the drying technique of this invention makes it possible, where necessary, to reduce the volatiles content of a polymer to below the detectable limit, e.g. <1 ppm, those skilled in the art are aware that in many cases it is sufficient to reduce the volatiles content, e.g. water, of synthetic polymers to less than 5000 ppm, more preferably about 3000 ppm. The advantages of this invention are still obtained where drying is suspended at these higher levels of volatiles content e.g. 3000 ppm.

For example, the polymer bulk temperature under these conditions is only about 180—190°F. as compared to about 375—500°F. when conventional techniques are used for drying to these levels. As had been pointed out, the advantages obtained as a result of the lower temperatures are improved appearance, e.g. snow-white rather than off-white or amber color, and broader molecular weight distribution. Additionally, the polymers exhibit higher tensile strengths and modulus of elasticity.

Though the process has been described in terms of removing water, it is evident that it is applicable to any polymer process which requires the removal of a vehicle so long as the vehicle (water or organic solvent) is polar. The wet polymer need only be delivered as a powder, crumb or pellet to the microwave oven. The term "polar vehicle" as used in this specification and claims means water or a polar organic solvent, i.e., organic solvents with a dielectric constant greater than 4.0.

WHAT WE CLAIM IS:—

1. A process for removing a polar vehicle (as defined) from an essentially non-polar synthetic polymer containing the polar vehicle which comprises:

(a) transferring the synthetic polymer containing the polar vehicle to a conveying means; and

(b) passing said polymer by means of said conveying means through at least one microwave resonating cavity operating at a microwave frequency of 900 to 30,000 MHZ for

- a period of time sufficient to reduce the polar vehicle content of said polymer to less than 5,000 ppm.
2. A process according to claim 1, wherein the polymer is in particulate form.
3. A process according to claims 1 or 2, wherein the polymer is passed through two microwave resonating cavities, the first operating at a microwave frequency of 915 MHZ and the second operating at a microwave frequency of 2450 MHZ, the period of time in the first cavity being sufficient to reduce the vehicle content of the polymer to less than 5 wt. % and the period of time in the second cavity sufficient to reduce the vehicle content of the polymer to less than 5,000 ppm.
4. A process according to any of the preceding claims wherein the polymer is passed through the cavity or cavities for a time sufficient to reduce the polar vehicle content of the polymer to less than 10 ppm.
5. A process according to any of the preceding claims, wherein the synthetic polymer when transferred to the conveying means has a polar vehicle content of 6-30 wt. %.
6. A process according to any of the preceding claims, wherein the polymer has been produced as a slurry in the polar vehicle.
7. A process according to any of the preceding claims wherein the synthetic polymer is styrene-butadiene rubber, butyl rubber, halogenated butyl rubber, polyvinyl chloride, polypropylene or polyisobutylene.
8. A process according to claim 7, wherein the polymer is butyl rubber crumb, the polar vehicle is water and the water content of the crumb is reduced by mechanical dewatering to 6-30 wt. % prior to being transferred to the conveying means.
9. A process according to claim 1 wherein the polymer is polyisobutylene in particulate form, the polar vehicle is water, the polyisobutylene particles when transferred to the conveying means have a moisture content of less than 5 wt. % and the time in the resonating cavity is sufficient to reduce the moisture content to less than 1 ppm.
10. A process according to claim 9, wherein the particles when transferred to the conveying means have a moisture content of 0.1 to 0.8 wt. %.
11. A process according to claim 9 or 10, in which the dry polyisobutylene is thereafter baled by compressing the polymer at a temperature of 140-250°F and a pressure of 800-3500 psig for 5-16 seconds.
12. A process for removing a polar vehicle (as defined) from an essentially non-polar synthetic polymer containing the polar vehicle, substantially as described with reference to the examples.
13. A process for removing a polar vehicle (as defined) from an essentially non-polar synthetic polymer containing the polar vehicle, substantially as described with reference to the drawings.
14. The product of a process claimed in any preceding claim.

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COMPLETE SPECIFICATION

1 SHEET

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the Original on a reduced scale*

